

NOVEL BEHAVIOUR OF CYCLOHEPTATRIENE

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SUMMARY

The reaction of cycloheptatriene with tantalum pentachloride gives a novel compound having the formula $\text{TaCl}_3(\text{C}_7\text{H}_7)_2$, in which cycloheptatriene is present as the cycloheptatrienyl anion.

INTRODUCTION

Cycloheptatriene and a number of its alkyl derivatives react with Group VI metal carbonyls giving orange red crystalline diamagnetic complexes of general formula (cycloheptatriene) $\text{M}(\text{CO})_3$ (where $\text{M} = \text{Cr}, \text{Mo}$ or W)¹⁻³. In the Group VI complexes cycloheptatriene behaves formally as a six π -electron donor with each double bond supplying two electrons to the metal, so that with six electrons from carbonyls, the metal attains the rare gas configuration. Complexes of the type $\pi\text{-C}_7\text{H}_7\text{-Mo}(\text{CO})_2\text{X}$ (where $\text{X} = \text{Cl}, \text{Br}$ or I) have been prepared by treating $\pi\text{-C}_7\text{H}_7\text{-Mo}(\text{CO})_3$ cation with the appropriate halide ion⁴. The iodo complex reacts with $\text{NaMn}(\text{CO})_5$ to give a dark green complex $\pi\text{-C}_7\text{H}_7\text{-Mo}(\text{CO})_2 \cdot \text{Mn}(\text{CO})_5$ containing a mixed metal-metal bond and with NaC_5H_5 to give an orange diamagnetic complex $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{-C}_7\text{H}_7$ ^{5,6}. In this complex the C_7H_7 group seems to function as a three π -electron donor, *i.e.*, as a substituted π -allyl group, in order that molybdenum achieves the rare gas configuration. The only metal of Group V with which the reactions of cycloheptatriene have been studied is vanadium. Cycloheptatriene reacts with $\text{V}(\text{CO})_6$ resulting in the formation (21% yield) of dark green diamagnetic π -tropylium vanadium tricarbonyl [$\pi\text{-C}_7\text{H}_7\text{V}(\text{CO})_3$]⁷. Reactions of cycloheptatriene with metal chlorides of Group V have not been so far reported. This paper deals with the reaction of cycloheptatriene with tantalum pentachloride resulting in the formation of bis-(cycloheptatrienyl)tantalum trichloride, a new complex in which cycloheptatrienyl behaves as an anion. Similar experiments with other halides and oxyhalides of Groups IV, V and VI are in progress and the results will be published in due course.

EXPERIMENTAL

Special precautions were taken to exclude moisture. Tantalum pentachloride was prepared by direct chlorination of the metal. Benzene dried with and distilled over sodium was further purified by azeotropic distillation.

TABLE I

INFRARED ABSORPTION SPECTRA^a (in cm^{-1}) OF BIS(CYCLOHEPTATRIENYL)TANTALUM TRICHLORIDE IN NUJOL MULL

3900	vw	1610	vw	1375	s
3800	vw	1575	m	1340	vw
3000	vs	1560	m	1315	vw
2400	s	1550	m	1015	vw
2160	vw	1540	m	720	vw
1715	vw	1465	s		
1650	vw	1425	(sh)		

^a vw: very weak; m: medium; s: strong; vs: very strong; (sh): shoulder.

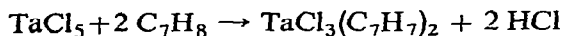
Preparation of bis(cycloheptatrienyl)tantalum trichloride

To 2.5 g of tantalum pentachloride in 200 ml of dry benzene, was added 1.29 g of cycloheptatriene. The contents were refluxed until there was no further evolution of hydrogen chloride. The brownish compound thus obtained was dried under reduced pressure. (Found: C, 35.52; Cl, 22.55; Ta, 38.30. $\text{C}_{14}\text{H}_{14}\text{Cl}_3\text{Ta}$ calcd.: C, 35.79; Cl, 22.69; Ta, 38.53%.)

The IR spectrum (in nujol mull) was recorded on a Perkin-Elmer Model 137 spectrophotometer, and the peaks are shown in Table 1.

RESULTS AND DISCUSSION

The positively charged ion C_7H_7^+ derived from cycloheptatriene by loss of a hydride ion has a closed shell of six π -electrons. Its salts are known as tropylium or tropylium salts. Hückel⁸ predicted that these salts would have aromatic character. The seven membered C_7H_7 ring has three bonding and four antibonding orbitals. Thus of the species C_7H_7^+ , C_7H_7 , C_7H_7^- only the cation has all its electrons in bonding orbitals and a closed electron shell, and thus should be the stable species of the three, but we have now shown that C_7H_7^- can be formed. Postulation of the formation of C_7H_7^- is consistent with the evolution of hydrogen chloride during the synthesis as shown by the following equation.



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